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Wood, liquefied in polyhydroxy alcohols as a fuel for gas turbines

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HIGHLIGHTS

- Fuel preheating required.
- Managable emissions.
- High turbine inlet temperature lower CO and THC.

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ABSTRACT

The paper reports foremost the results of a successful combustion of an innovative lignocellulosic biofuel in a gas turbine. The fuel was processed through liquefaction of lignocellulosic materials with polyhydroxy alcohols in an acid catalyzed reaction. The liquefaction process features: high efficiency, high liquid yields and inexpensive, easily available process equipment. For the purpose of this analysis the following were developed: an experimental gas turbine with internal combustion chamber, a preheated pressurized fuel supply system with swirl-air fuel injector and a heat exchanger to obtain high primary air temperatures. The paper gives results on the emissions of CO, THC, NO_x and soot. For the purpose of benchmarking the turbine was also run on diesel fuel. The paper presents analyses of the underlying phenomena with which it aims to provide guidelines for improvements in the fuel processing and in the experimental equipment. It has been shown that direct utilization of this innovative lignocellulosic biofuel gives promising results. Although the CO and THC emissions are higher compared to the benchmark diesel results it has been shown that both emissions decrease with increased turbine inlet temperature and with the increased fuel preheat temperature, due to a very high viscosity of the fuel. It is additionally shown that NO_x emissions are low and comparable to those of the diesel fuel, whereas soot emissions are very low for both fuels.

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1. Introduction

Although it is difficult to compete with fossil fuels in terms of performance and costs, second generation biofuels are already becoming more popular with the main reason being availability from low quality residual biomass and other lignocellulosic materials. Their inoffensive production in comparison to food competitive feedstock and their carbon neutrality is also beneficial as presented in [1–3]. In the past, lignocellulosic materials have been used in relatively simple combustion devices. To exceed a relatively low maximum efficiency of a wood boiler (26% [1]), a shift towards liquid and gaseous fuels is necessary which will enable conversion of lignocellulosic materials in piston engines, gas turbines and combined plants consecutively. Another advantage of liquid fuels is their superior transportation ability as they offer high energy density and are easy to manipulate with.

In addition to the biological, numerous thermo-chemical procedures have been developed to convert solid lignocellulosic material into liquid. Different types of pyrolysis (thermal decomposition), which are extensively reviewed in [4], decompose biomass to generate vapors, aerosols and char. Different types of pyrolysis exist, one of them, flash pyrolysis, is optimized for generation of liquid product. Crucial parameters of flash pyrolysis include high heating and heat transfer rates, precisely set residence times and rapid cooling. Heating rates up to 1000 °C/s have been reported [4]. Rapid heating and quenching produces intermediate products which condense before they break down into gaseous products or before they further react and form molecules with high molecular mass. Main product is frequently named bio-oil, which features physical properties in the following ranges: HHV 16–19 MJ/kg, density

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around 1.25 kg/L, moisture content 15–20% and oxygen content 35–40% [1]. The main advantage of bio-oil is its very low ash and sulfur content as only heat is used to depolymerize lignin, cellulose and hemi-cellulose. When considering all aspects of the conversion process, the overall efficiency is fairly low. Production of bio-oil from wood has the overall biomass to liquid conversion efficiency in the range of 72–80%, depending on the cellulose content [4]. If feedstock with high lignin content such as bark is used, the process efficiency is around 60–65% [4]. Taking into account water content, overall efficiency of the process to produce water free combustible liquid easily comes down to 50%. Moreover, expensive and technically complicated process equipment is needed for flash pyrolysis, since the temperature ranges from 600–700 °C and precise residence times of biomass are required during the process. Besides, 15–25% of solid char and 10–20% of noncondensable gasses are produced as byproducts.

Biocrude is a product of liquefaction with subcritical water (hydrothermal liquefaction) – detailed mechanisms and technologies of the hydrothermal liquefaction are given in [5]. The conditions for initiating liquefaction reactions are less demanding than for initiating pyrolysis reactions, with temperature from 277–377 °C and pressure from 0.7–2.0 bar [1]. Depending on the type of the catalyst used, liquid yields in the range of 58–96% can be achieved. Biocrude has a HHV 30–36 MJ/kg and 10–20% oxygen content and it is in a non-flowing state at ambient temperature. Detailed specification can be found in [6].

In addition to heavy fuels produced from lignocellulosic biomass, bio ethanol is emerging, produced from either gasification-synthesis or gasification–fermentation as well as hydrolysis–fermentation [7]. Ethanol is considered as a light fuel which can be directly used in conventional engines by blending it with gasoline. However, the above ethanol production processes are still in development stage and thus their conversion efficiency is low as lignin cannot be broken down. Moreover, high initial investments are needed for production plants [7].

The innovative lignocellulosic liquid fuel being considered in this paper is produced from wood or other lignocellulosic materials by liquefaction in the presence of polyhydroxy alcohols. Such a process is usually carried out at temperatures of 160–200 °C, at ambient pressure and in the presence of acid catalyst. Product is frequently referred to as a liquefied wood (LW) [8–13]. Benefits of this liquefaction process arise from a significant process simplification in comparison to other aforementioned processes and from the possibility to use residual glycerol from biodiesel production in the production process of the LW. Liquefaction is possible up to 1:1 ratio of alcohols to wood. Low-price glycerol is widely available from transesterification of vegetable oils and could be used for this purpose if residual base catalyst is removed from it. Base, present in the crude glycerol inhibits liquefaction reaction as acid catalyst is neutralized, so utilization of crude glycerol should be done with caution. However, use of raw glycerol would increase the share of renewable input material to around 98% if biomass and glycerol are considered as fully renewable and only acid catalyst is a non-renewable reactant. Since purification of glycerol is relatively expensive process, efforts are being made to replace pure glycerol used in pilot production with crude or partly refined glycerol. Simple and highly efficient liquefaction process is mainly a consequence of low processing temperature which lowers the energy input for liquefaction to as low as 0.45 MJ/kg [12]. With carefully selected reaction parameters, up to 99% of dry input biomass is completely converted into liquid. With such efficiencies of conversion solid residue never exceeds 0.5% (if 1:1 ratio of glycerol to wood is used) of the final product which is also beneficial for filtration costs. After completed liquefaction process, subsequent cooling of the fuel from only 160 °C to ambient temperature represents a relatively small heat loss in comparison to the cooling of the bio-oil and biocrude, making LW especially suitable for transportation and distribution to the end user.

Liquefied wood can be used as bonding material in production of particle boards [8] and as raw material in production of polyurethane foams. Moreover, there was a proposal for use of hydrogenated LW as a fuel in [14], however it has not yet been tested. Hydrogenation of LW is an additional upgrading process, which makes such fuel expensive and complicated to produce. Unlike most of the biomass derived liquid fuels, production of pure liquefied wood is economically viable and could be competitive to petroleum fuels for certain applications (e.g. co-generation plants, district heating applications). LW features a relatively inexpensive feedstock and also a short chain from the producer to the final user, which might make this product profitable, even if processing price is higher than that of petroleum fuels. Until now, to our knowledge, no research has been done on the combustion of pure, non-upgraded LW in gas turbines yet. Therefore this paper offers an insight into potential usefulness of this innovative LW as a low cost second generation biofuel.

2. Materials and methods

2.1. Liquefied wood

2.1.1. Fuel processing

Liquefaction of wood was carried out in a stainless steel 200 L pilot reactor equipped with a mechanical stirrer, a weight scale and a heater. Glycerol and diethylene glycol were used as the liquefaction agents and p-Toluensulfonic acid (pTSA) as the catalyst. From a wide variety of recipes yielding different LW properties the one featuring most favorable properties for the use in gas turbines was selected. In particular, one of the main goals was to produce LW with acceptable viscosity, since high viscosity of some recipes restricted its usage in the gas turbine. The viscosity was mainly reduced by three mechanisms. First, by limiting the upper content of wood, since degradation products generally still include molecules with molar mass higher than glycols. Second, by substituting half of the glycerol with polyhydric alcohol which featured lower viscosity. Third, by steering the reaction time in a way that lowest solid residue and lowest acidity of the LW were achieved, since reaction time significantly influences these two parameters [14]. When liquefaction parameters were set, wood flour from European spruce stem was added to glycol mixture in proportion (1:3) and 3% of pTSA, based on a mass of glycols was added. The mixture was held for 3 h at 180 °C while being constantly stirred. Low quantity of solid residue was later removed by means of filtration through a 100 μm mesh. Liquefaction time has a major influence on the residue concentration as polycondensation of the products occurs after a longer reaction time. Liquefaction yield is relatively insensitive to wood type if reaction duration is precisely timed. After that, liquefaction products of some types of wood are more prone to condensation and re-formation of solid residue, while other types show very low condensation rates [15]. Residue comes from reactions between cellulose and lignin disintegration products and can be avoided if only lignin or only cellulose is used [9]. Liquefaction process is highly complex from chemical point of view. Major intermediate substances and major final products during cellulose liquefaction are presented in [9]. Study conducted in [11] characterizes reaction pathways for liquefaction of lignin and combination of lignin and cellulose.

2.1.2. Fuel properties

Dynamic viscosity of the product was measured after initial cooling using a rotational viscometer. Additionally, elemental composition was measured with the modified Pregl–Dumas method,

while the HHV was measured using a bomb calorimeter, calibrated by combustion of certified benzoic acid. The LHV was then calculated as follows: LHV = HHV [MJ/kg]−0.21813 H[%] [MJ/kg] [16].

LW consists of a wide variety of sugars, oligomers, carboxylic acids, aldehydes, ketones and alcohols [9,11]. All of these highly oxygenated compounds contain cyclic structures and thus feature high autoignition temperatures. Elemental composition in Table 1 is revealing high oxygen content, which almost halves the heating value with respect to pure non-oxygenated hydrocarbon fuels. However, oxygen content also accounts for a relatively low stoichiometric ratio, 6.8:1 and thus the energy density of the air–fuel mixture of the LW is comparable to that of the crude oil distillation products at the specific equivalence ratio. This is also the reason for high adiabatic flame temperature (2135 °C) of LW since H/C ratio of LW is very close to that of diesel fuel. Moreover, high density (1.3 kg/L) of the LW results in a relatively high volumetric energy density of 28.5 MJ/L (35.8 MJ/L for diesel fuel). Similar to other fuels derived from biomass, liquefied wood has low sulfur content and, based on the feedstock analysis, it also had low ash content. Major source of sulfur is pTSA, which accounts for less than 0.5%. If pure glycols are used in liquefaction, the only source of ash is wood flour. Variations in ash content for various tree parts is presented in [17]. Ash content also varies with the type of wood and its growth conditions and accounts for approximately 1000 ppm in spruce wood where calcium accounts for 70% of ash.

Liquefied wood is immiscible with non-polar liquids, however it can accept small amounts of water before precipitate occurs. It mixes well with alcohols, therefore various blends can be made, while by mixing with petroleum derived fuels only emulsions can be produced. It can be easily removed from process equipment using solely hot water. Thereby handling is seriously simplified in comparison with petroleum derived heavy fuels.

Although all of the above properties closely resemble those of flash pyrolysis oil, as presented in Table 1, the production process itself is closer to hydrothermal liquefaction than pyrolysis. When comparing flash pyrolysis to hydrothermal liquefaction and liquefaction in polyhydroxy alcohols, only the latter two can be considered as a direct liquefaction processes, since main liquefaction mechanism is solvolysis, while the pyrolysis is a thermolysis process. The main difference between biocrude and liquefied wood, which influences preparation of combustible mixture is higher oxygen content accompanied by low heating value of the LW. This can mainly be attributed to the fact that almost no gas is released during the reaction in alcohols and to the fact that solvent used in the LW reaction features higher O/C ratio. In case of biocrude H_2, CO_2, CH_4 and CO are released which lowers oxygen content and also decreases conversion efficiency of the biocrude, while high O/C ratio of glycerol and diethylene glycol versus water used in hydrothermal liquefaction elevates the mass fraction of oxygen in the LW.

Depending on the formulation used in production, numerous grades of viscosity can be obtained [20]. Reactant ratios described in 2.1.1 gave a product with viscosities presented in Fig. 1, although even lower values can be achieved by lowering wood content or replacing even more glycerol with diethylene glycol as discussed above. It is also interesting to note that LW is characterized by the less pronounced decrease in viscosity at elevated temperatures compared to heavy petroleum fuels.

Utilization of biofuels in gas turbines is rapidly advancing in the recent years, which also broadens the range of acceptable fuel properties. In terms of viscosity, it is currently considered that sufficient atomization of liquid fuels for gas turbines can be achieved with fuels featuring kinematic viscosities of up to 15 mm^2/s [21], while some authors propose values of 12 mm^2/s [2] or even lower 10 mm^2/s [22,23]. In terms of the calorific value, fuel should meet the requirements within 5% of the target value [21], which also depends on the design of a gas turbine. In line with the objective of this study, which is exploring potentials and possibilities of utilizing LW in the gas turbine, a laboratory scale flexible experimental rig that is adapted to wide range of chemical and physical fuel properties, including high viscosity and low heating value is used. Extent of fuel system and combustion chamber modifications on professional turbines is greatly dependent on suitability of the turbine to burn heavy fuels. Possibilities exist that turbines designed

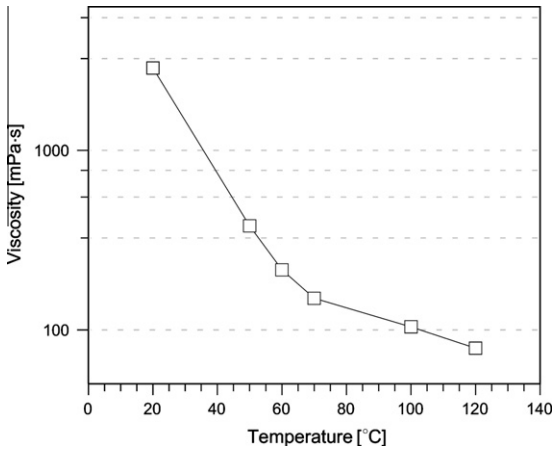

Fig. 1. Viscosity variation over temperature for liquefied wood.

Table 1
Major properties of the liquefied wood, compared to bio-oil, biocrude and diesel fuel.

Product	Liquefied wood	Biocrude [5,6,18]	Bio-oil [1,4]	Diesel fuel [19]
Color	Black to dark brown, depends on raw material and formulation used	Black to dark brown	Black, dark red to brown, depends on feedstock and pyrolysis mode.	
Miscibility	Miscible with polar solvents, immiscible with non-polar liquids (e.g. petroleum derivatives, fats and oils), accepts small amounts of water before precipitate occurs	40% water soluble	Miscible with polar solvents, accepts 15–50 wt.% of water	
Density [kg/L]	1.3	1.1	1.2	0.83
C [wt.%]	47.60	76.7	41.7	86.2
H [wt.%]	7.98	7.1	7.7	13.7
N [wt.%]	0.19	<0.1		
S [wt.%]	0.89			
O [wt.%]	Rest (43.34)	16.1	50.3	
Stoichi. ratio	6.8:1	10.7:1	5.3:1	14.5:1
HHV [MJ/kg]	21.9	36.5	19.1	46.1
LHV [MJ/kg]	20.2	35	17.4	43.1
pH	Below 3.5	6–8.5	2.8	5.6

to utilize pyrolysis oil, would need minimal changes as properties of liquefied wood are close to those of pyrolysis oil.

Stability at room temperatures of the LW was carefully studied over several months. There were no changes observed regarding the viscosity or any other physical changes. However, when the LW is subjected to elevated temperatures, for example, higher than 120 °C, the viscosity increases with time. This indicates the presence of the polymerization process. The neutralization would increase the stability even at that elevated temperatures as the acid catalyst would be neutralized and the rates of reactions would be substantially reduced. However, even in the case of pure LW, the polymerization at temperatures higher than 120 °C is a slow process, observed only after several hours.

2.2. Experimental setup

2.2.1. Fuel supply system

Due to a relatively high viscosity of the liquefied wood, preheating is required to achieve sufficient spray atomization quality of the fuel. Atomization might also be enhanced by adding ethanol or any other polar solvent, since products of liquefaction are completely immiscible with non-polar liquids (e.g. petroleum derivatives, vegetable oils). However, addition of ethanol leads to an increase in the fuel production costs and to possible combustion related problems [16] thus the objective is to burn pure liquefied wood.

Preheating system shown in Fig. 2 was designed using suitable materials to withstand acidic medium as pH of LW is under 3.5 [15]. LW was held in a pressurized container at ambient temperature. The quantity of the LW that was consumed during the combustion was continuously supplied from the container to the fuel heater with pulse width modulation control. Circulation of the medium through the filters and through the return line to the heater was provided by a gear pump. Filters, developed exclusively for filtration of LW were used to capture larger inclusions which could endanger fuel injection system or the hot path components of the gas turbine. The filter elements were accessible and could be cleaned by mechanically scraping off the captured solids. Coriollis type flow meter was used for fuel flow supervision which also allowed for in-line density measurements. Majority of the LW flow was circulated to establish homogenous temperature throughout the system, while smaller portion of the LW flow was fed to the combustion device. To avoid vapor formation and to avoid any losses of volatile components the system was kept under elevated pressure, although most of the lighter components should already had evaporated during the liquefaction reactions where temperature exceeded 160 °C. It might be noted that final phase of wood liquefaction process includes quenching of liquefaction reactions. It is therefore beneficial that during the fuel preparation, temperatures throughout the fuel supply system are kept well under 150 °C. When this temperature is reached, rate of liquefaction reactions significantly increases as catalyst in form of pTSA is still present in the fuel. This effectively means lengthening of liquefaction reactions time which increases solid residue re-formation as described in 2.1.1. However, short boosts on higher temperatures should not present major problems as reactions are generally slow and rate of residue formation is low.

LW temperatures throughout the fuel supply system were measured on several characteristic locations using *K* type thermocouples and by platinum resistance thermometer. Pressure monitoring allowed for identification of the rate of filter obstruction buildup and for supervising the fuel nozzle operation point. Remotely controlled main pressure valve was used to set the desired injection pressure, which simultaneously determined the pressure level in the fuel supply system. Generally, all temperatures were kept between 80 °C and 110 °C and all pressures in the range of the fuel nozzle requirements (around 2.5 bar).Fluctuations in the combustion chamber pressure had minor influence on the injected fuel quantity because fuel supply line was coupled directly to the feed arm of the gas turbine. As pressure in the fuel supply system was kept at constant level, differential pressure on the fuel nozzle discharge orifice was adversely affected by the combustion chamber pressure. This type of fuel supply system allowed for self-correcting the operating parameters of gas turbine. This means that fuel quantity was increased due to increased pressure difference if combustion chamber pressure decreased due to any reason, which lead to increased turbine enthalpy flow and resulted again in higher combustion chamber pressure and restoration of other desired parameters. With carefully designed system, minor inhomogenities of fuel properties (namely calorific value) could also be overcome.

2.2.2. Experimental gas turbine

Experimental test rig consisting of an automotive turbocharger, a jet engine combustion chamber (Fig. 4) and a heat exchanger (Fig. 3) was developed to test the combustion performance of different fuels. A free spinning turbocharger was used in the test rig and thus combustion characteristics of the LW were assessed by

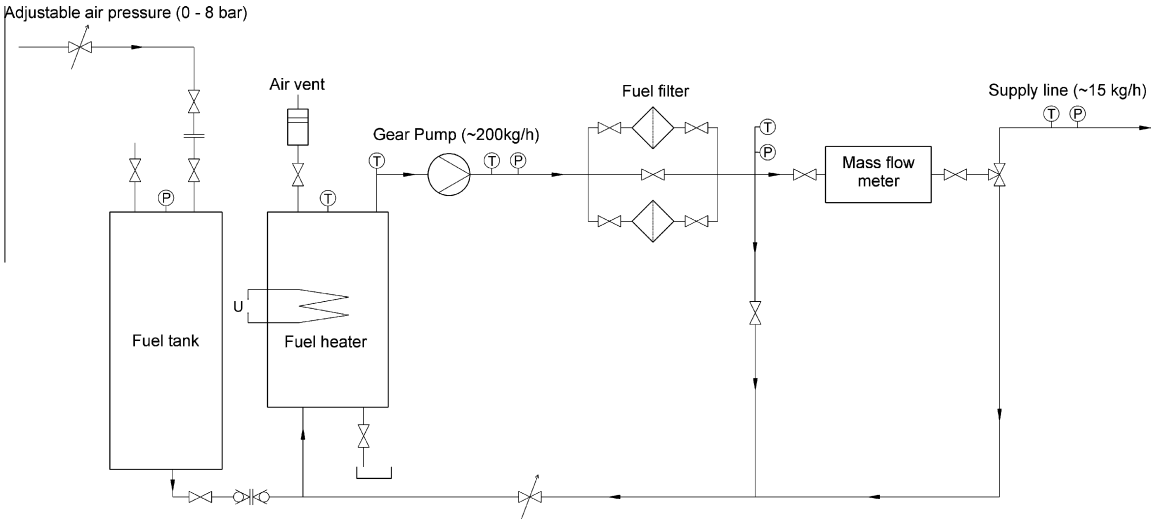

Fig. 2. Fuel preparation system with indicated positions of sensory equipment.

thermodynamic and exhaust emission measurements and not by measuring the shaft power. Thereby presented results cover much broader range of data relevant for assessing characteristics of the LW as a fuel. In line with these objectives operating point of the turbocharger was in addition to the fuel flow steered also by the position of the butterfly valve downstream of the turbine, which influences the turbine backpressure. Settings of the butterfly valve were maintained in the same position throughout the combustion experiments to allow for comparative measurements. Compressor intake air flow, temperature and humidity were measured at the intake duct. Pressure was additionally measured downstream of the heat exchanger. Throughout the air stream path temperatures were measured on several locations (shown in Fig. 3) using *K*-type thermocouples. Recuperation intensity was controlled with the exhaust gas flow through a recuperator. For visual inspection of the flame position quartz windows were used. Due to heat recuperation it was possible to attain intake air temperatures at the combustion chamber entry in excess of 400 °C thus effectively reproducing conditions present in a typical microturbine.

As it was presented in Fig. 1, kinematic viscosity of the LW is 61 mm^2/s at 120 °C. The choice of fuel nozzle is therefore of great importance. Air-blast atomizers feature a series of desired characteristics: they are relatively insensitive to fuel viscosity, they have large flow passages that tolerate possible solid impurities in tested fuels and atomizing air also works as a thermal barrier to prevent coking of fuel on the internal surfaces of the nozzle. The choice of the air-blast atomizers is further justified by the fact that mixing of atomizing air and fuel suppresses the soot formation and reduces the flame radiation [21]. Due to very high fuel viscosity, swirl-air design of the nozzle was chosen. Besides the spray breakup caused by the swirling air flow in the mixing chamber, fuel atomization is additionally promoted by double jet surface impingement accompanied by even larger quantities of atomizing air than in conventional air-blast atomizers. Atomizing air flow was in the range of 0.15 m^3/min and it was varying slightly with the fuel pressure as stated by the nozzle manufacturer [24]. Design of the nozzle is not optimized for the use in gas turbines with high fuel preheat temperatures because it features a relatively large frontal area, which substantially increases heat transfer to internal parts of the nozzle. Moreover, convective heat transfer to the feed arm and the nozzle was also high due to high intake air temperatures (in excess of 400 °C) and due to a highly turbulent flow field. The feed arm was therefore insulated with ceramic fibers to avoid excessive heating of atomizing air. This measure was not sufficient to prevent fuel coking on the nozzle. To minimize also the radiative heat transfer that accounts for over 95% of heat flux to the nozzle [21], a ceramic protection for large frontal area was applied. Ceramic putty with good refractory properties was used to fabricate

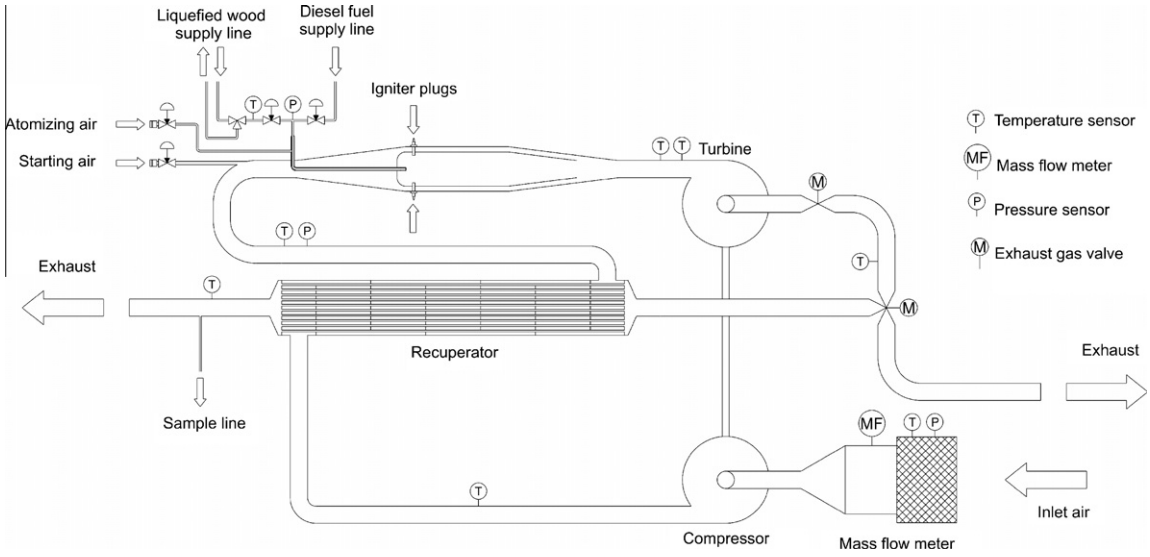

Fig. 3. Simplified construction drawing of the testing site with locations of temperature and pressure sensors, including location of probe for gas sample collection.

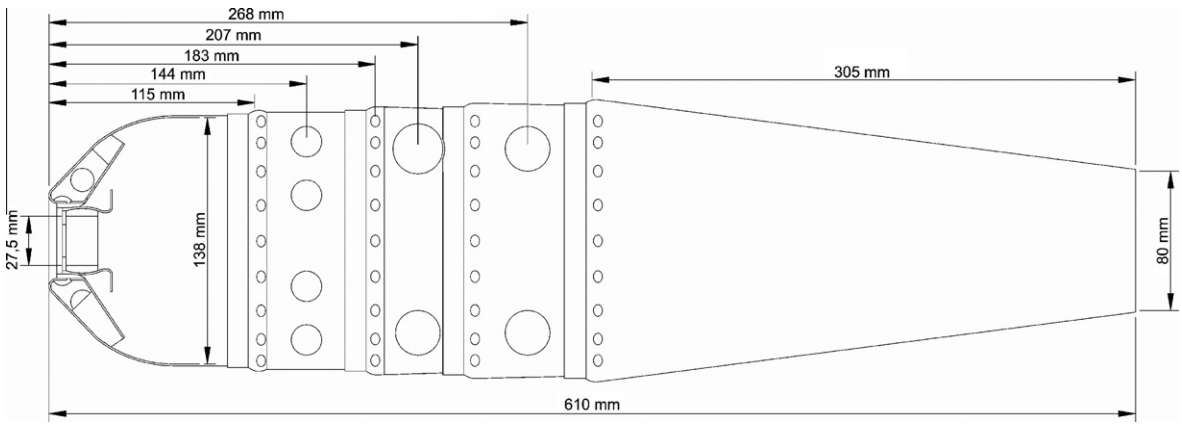

Fig. 4. Cross section of combustion chamber.

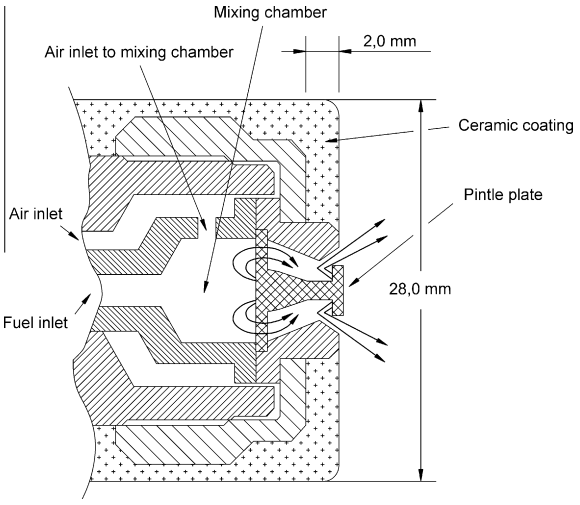

Fig. 5. Cross section of swirl-air fuel nozzle [24], upgraded with ceramic coating to reduce heat transfer.

thin protective layer that significantly reduced nozzle surface temperatures. Basic schematic of the nozzle with the insulation is presented in Fig. 5.

2.2.3. Exhaust gas measurements

Concentrations of CO_2, H_2O, CO, THC and NO_x were measured using "Horiba OBS 2200" constant flow measurement device with the following measuring ranges: CO 0–0.5 vol.%, CO_2 0–5 vol.%, THC 0–1000 ppm C, NO_x 0–1000 ppm [25]. Standard gasses were used to set zero and span calibration settings of the analyzers. Gas samples were collected in exhaust pipe downstream of the heat exchanger and fed to the analyzer through a heated pipe (190 °C) to avoid any condensation of combustion products. Emission equipment paper filter element was used to remove particulate emissions. Smoke emissions were measured with AVL opacimeter, which pumps constant exhaust gas flow through illuminated cell. Opacity of the sample then defines the degree of smoke emissions. Filter cartridges from emission equipment turned out to be an excellent qualitative comparative indicator of particulate emissions at different operating conditions.

2.2.4. Experimental procedure

Startup and preheating of the experimental gas turbine was carried out with diesel fuel. Afterwards, fuelling was switched to the LW. Shutdown procedure was again done with diesel fuel to prevent polymerization of the LW in the fuel nozzle. Numerous researchers in the area of biomass based liquid fuels report that combustion of ethanol in the final stage of experiments was used to flush the pipework and fuel nozzle. In a case of the experimental turbine used for the combustion tests of LW, this step was proven to be unnecessary. The use of PTFE tubing enabled satisfactory flushing even when diesel fuel was used. Additionally, recuperator was bypassed during startup and shutdown to minimize pressure losses and to cool components upstream of the combustion chamber. Each operating point of the experimental gas turbine was stabilized until constant readings of operating parameters were reached. Each operating point was stabilized for approximately 20 min, what accounted for 3.5 h overall operation time to collect the desired data. Long term operation in excess of 800 h was possible without noticeable problems and with stable emission readings. To ensure that the gaseous exhaust emissions were measured at similar operating conditions as the smoke emissions, samples were drawn at the same time through separate sample lines. The equipment for measuring gaseous emissions was drawing constant sample flow of around 3 L/min, which allowed for a precise calculation of filtered and analyzed exhaust gas quantity.

3. Results and discussion

In this section the results of exhaust emissions measurements are analyzed for different temperatures of the LW and for different turbine inlet temperatures (TIT). Comparative measurements with diesel fuel were carried out to obtain benchmark data, as it is the most widespread liquid fuel for such applications. Moreover, the analyses of comparative results revealed specific constructional requirements (for combustion chamber design) needed to lower the emissions when burning LW as discussed in the next section. The emphasis was on the emissions of: total hydrocarbons (THC), carbon monoxide (CO), nitrogen oxides (NO_x) and smoke. Other potentially harmful emissions were not measured as it was hard to accurately define which compounds to look for. Due to a very complex composition of liquefied wood, even precursors for toxic emissions are so far unknown.

Matrix of the experiment was defined considering the characteristics of the LW and experimental equipment. Fuel preheat temperatures were thereby kept in 90–110 °C range, depending on target operating point, while TIT was varied from 750 °C to 850 °C. Other parameters resulted from the fueling and from the compressor and the turbine characteristics as well as pressure losses along the air stream path. As can be seen in Table 2, operating parameters closely resemble conditions present in a commercial microturbine engine. For each fuel preheat temperature three different TIT were set and emissions were measured. All key values of the operating points where exhaust emissions were measured are presented in Table 2. It can be noticed that higher turbine inlet temperatures come with increased air flow which increases pressure losses along air path and thereby increases equivalence ratio.

Combustion efficiency (CE) was calculated on the basis of CO and THC emissions and corrected to 0% O_2 to eliminate the effect of excess air, by employing the following equation: CE[%] = 100%−((CO[%] + THC[%])/EQR). In all analyzed operating points combustion efficiency exceeded 99.77% This was achieved despite the fact that the viscosity of the LW is far above the value recommended for the use in gas turbines as presented in 2.1.2. The detrimental effect of high viscosity was thus compensated by the employment of the Swirl-air nozzle and the high oxygen content in the fuel. It is speculated that combustion efficiency is owed to the high evaporation rate and the presence of OH radicals since the OH radicals are essential for CO oxidation reactions [26]. High concentrations of the OH species in the flame zone arise from numerous oxygen atoms being available as well as from high hydrogen to carbon ratio of LW (2.0 for the LW compared to 1.9 for diesel fuel).

It was furthermore noticed that temperature of the fuel slightly influenced operating parameters at defined TIT. At lower fuel temperature slightly higher fuel mass flow was required to maintain the same turbine enthalpy flow. The difference in energy input is mostly needed to account for heating of the fuel, which, in this case happens inside the combustion chamber. Very small differences in fuel mass flow were observed, i.e. around 0.25% of fuel mass flow for 10 °C difference in fuel temperature and they are very close to the measurement uncertainty.

3.1. Effects of the fuel temperature

Viscosity of the LW has a strong temperature dependency as shown in Section 2.1.2. CO and THC emissions decrease with the increased fuel preheat temperature (Fig. 6). This is mainly the consequence of two phenomena: Firstly, the lower viscosity enhances

Table 2
Gas turbine operating parameters, defined by turbine inlet temperature during emissions measurements.

Fuel @ temperature [°C] – TIT [°C]	Intake air temperature [°C]	Combustion chamber air temperature [°C]	Turbine inlet temperature[°C]	Turbine outlet temperature [°C]	Compressor pressure ratio	Air mass flow [kg/h]	Atomizing air pressure [bar]	Fuel supply pressure [bar]	Fuel mass flow [kg/h]	Fuel temperature [°C]	EQR
D2@20–750	20.1	412.9	747.9	631.0	2.06	683.4	6.49	1.63	6.25	20.5	0.133
D2@20–800	21.7	441.7	805.8	671.2	2.28	752.4	6.47	1.82	7.63	20.6	0.147
D2@20–850	23.0	465.9	850.5	704.6	2.44	793.8	6.48	1.96	8.68	20.4	0.159
LW@110–750	23.4	418.1	752.1	630.3	2.04	672.8	6.49	2.04	13.58	107.5	0.137
LW@110–800	24.2	449.2	808.7	674.2	2.31	756.3	6.47	2.32	17.34	110.1	0.156
LW@110–850	22.5	472.4	854.0	707.5	2.59	822.9	6.47	2.62	20.93	106.9	0.173
LW@100–750	17.2	415.0	746.3	624.1	2.13	702.5	6.47	2.13	14.08	99.4	0.136
LW@100–800	17.9	438.0	798.3	657.5	2.36	771.2	6.47	2.41	17.20	101.0	0.152
LW@100–850	18.6	465.8	853.8	698.1	2.59	830.5	6.48	2.69	20.72	99.2	0.170
LW@90–750	17.7	414.0	743.2	621.2	2.13	703.4	6.49	2.23	14.16	90.3	0.137
LW@90–800	17.1	436.0	800.2	657.2	2.37	775.9	6.48	2.56	17.59	90.3	0.154
LW@90–850	19.2	466.9	849.5	699.0	2.55	817.3	6.49	2.76	20.12	89.1	0.167

formation of more intense instabilities on the liquid film, which then promote primary spray breakup, and secondly, the lower surface tension enhances secondary droplet breakup. Therefore, higher fuel preheat temperature results in a faster evaporation rate and in a faster and more homogeneous air–fuel mixture formation which is beneficial to combustion efficiency. In regions where the mixture strength is too weak to support combustion and in rich combustion areas products of incomplete oxidation such as THC and CO occur. Higher THC emissions compared to those of D2 fuel can also be attributed to the insufficient residence time of the mixture in the primary zone of the combustion chamber, or even to some non-evaporated droplets, which allow ignition resistant hydrocarbons to cross the high temperature zone without reacting or reacting only partially and thus contributing to the THC emissions. Liquefaction reactions pathways indicate that liquefied wood contains a large amount of cyclic hydrocarbon molecular structures with high ignition energy, which confirms previously mentioned source of THC emissions.

CO emissions are usually the result of reaction quenching and local flame extinction when postflame products cool sufficiently by either becoming entrapped in liner cooling air or diluted air and are therefore clearly promoted with the mixture's shorter residence times in the combustion chamber. This is also the consequence of the delayed breakup of cyclic hydrocarbons. Short residence time can also arise from insufficient atomization that produces larger droplets which, in combination with high fuel density, contributes to the increased penetration of fuel droplets and their late evaporation. All these effects shorten the residence time of the prepared mixture and promote the reaction quenching close to the combustion chamber walls thus resulting in higher emissions of CO.

Reduction of THC and CO with elevated fuel temperature is clearly visible in Fig. 6. The mechanism of this reduction can easily be extracted from the above analysis. Higher fuel temperature lowers its viscosity, which then reduces Sauter mean diameter (SMD) of the droplets. Smaller droplets effectively increase evaporation rate which then leads to more homogenous mixture formation and thus lower CO and THC emissions. However, the measured reduction of these two pollutants with increased fuel temperature is not substantial. This can be attributed to the relatively low sensitivity of the atomization performance of the nozzle on the fuel viscosity. This again confirms the suitability of the chosen nozzle for use with LW.

At a given TIT the diesel fuel mass flow is roughly half of the mass flow of LW, which is in agreement with the calorific values of the fuels. Additionally, these quantities are varied to attain target TIT. Because Swirl-air nozzle uses internal mixing chamber, the flows of fuel and atomizing air are interdependent. Increased fuel flow reduces atomizing air flow, so by varying TIT, quantity of atomizing air is also varied. It was observed that large quantities of atomizing air accompanied by the fine atomization and high nozzle surface temperatures, which promote evaporation of the fuel inside the nozzle, provide notable degree of premixing. Moreover, due to the very high oxygen content in LW (43%) it is not surprising that the blue flame front, which is characteristic for premixed mixtures [21], was observed in close proximity of the fuel nozzle. The difference in atomizing air quantity is estimated to be relatively small therefore the effect of different rates of premixing should be negligible at this point. However, close proximity of the flame could also contribute to the coke formation at high preheat temperatures as these conditions improve atomization and further improve the air–fuel mixing. Additionally, unexpected rise in CO and THC emissions is visible at high fuel preheat temperature, namely 110 °C and high TIT. Due to the fact that thermodynamic settings at fuel preheat temperature 110 °C equal to those at other two fuel preheat temperatures it can be concluded, that high fuel preheat temperature might be the main parameter influencing combustion phenomena. Because fuel is functioning as a heat sink for heat, transferred through external surfaces of the fuel nozzle, radiation from the flame at high TIT could easily elevate the temperature of the fuel to coking point, which is with 110 °C fuel temperature, closer than for lower fuel temperatures. Carbon buildup on the orifice then deteriorates atomization quality so much it becomes visible on the emissions readings. This is done by the occurrence of off center spray, which, in combination with high fuel density and large droplets, significantly increases penetration depth of fuel droplets. This leads to the impingement of the fuel droplets on the liner walls causing coke build up which is usually followed by a gradual burn out yielding high CO and THC concentrations. Moreover, it is not uncommon for pieces of coke to break off and continue their way through hot path components. This phenomenon is characterized by a low frequency acoustic disturbance and by instantly increased particulate emissions. Due to the fact that stable operation can easily be restored by lowering fuel mass flow or fuel temperature it is very unlikely that such events are the consequence of rapid fuel ageing under high temperatures. This thesis is supported also by the fact that LW is exposed to even higher temperatures during its production process.

Therefore the high CO and THC emissions are to a large extent related to the combustion chamber geometry and the flow field in the combustion chamber. These were not optimized for the use of the LW and thus the residence time of the mixture in

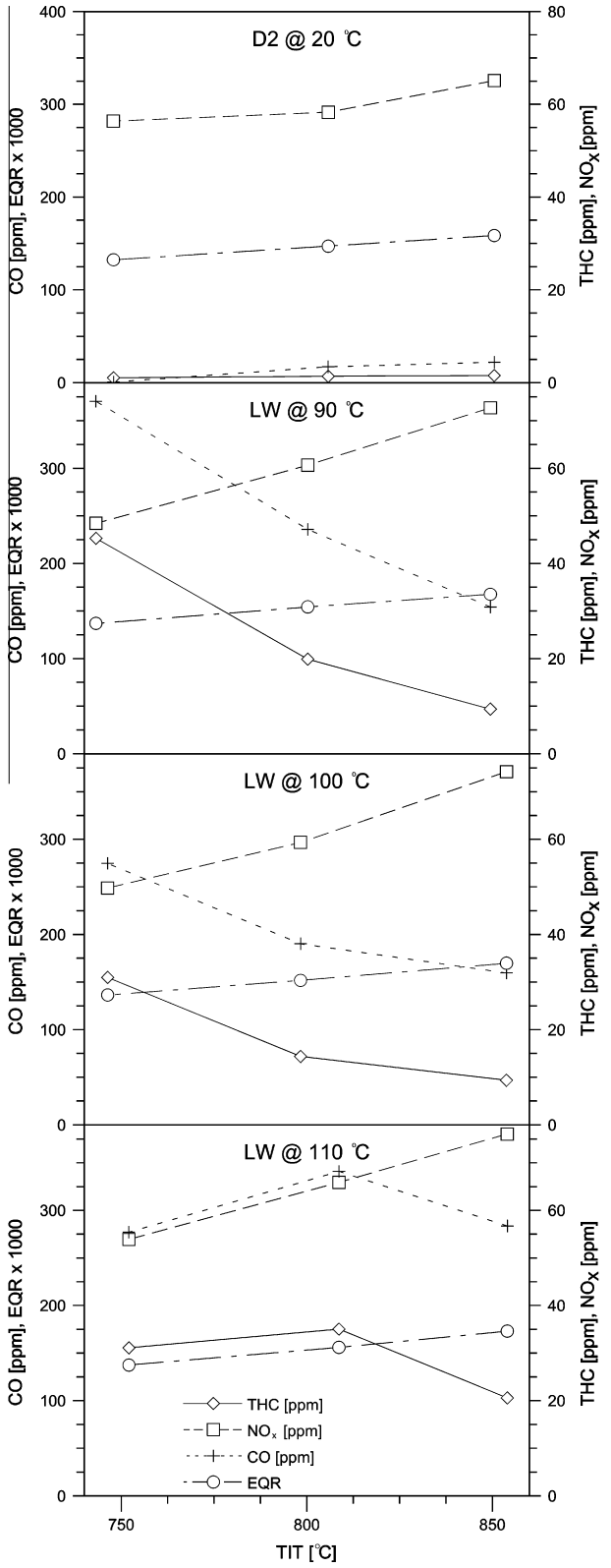

Fig. 6. CO, NO_x and THC formation for liquefied wood and diesel fuel (labeled "fuel type @ preheat temperature") as a function of turbine inlet temperature.

primary zone of the combustion chamber was insufficient. As presented in [21], only a fairly narrow range of equivalence ratios exists where low levels of CO can be achieved. At low EQR, slow rate of oxidation is associated with low combustion temperatures which promote CO formation. At high EQR, flame temperature rises and CO formation becomes promoted by chemical dissociation of CO_2. It is therefore of significant importance that combustion chamber is carefully designed for a specific fuel to assure that EQR in primary zone is in the appropriate range.

The increase in NO_x concentration between 90 °C and 100 °C of fuel preheat temperature is not sufficient to draw any conclusions on the atomization quality. However, similar mechanism as for CO and THC emissions might also be used to explain slightly higher NO_x emissions at 110 °C, since coke formation on the fuel nozzle and resulting poor atomization of LW increases the bulk exit NO_x [27].

It is therefore very important to determine the optimum fuel preheat temperature, which depends on the type of the fuel nozzle, on the combustion chamber dimensions and on the operating conditions. For the analyzed experimental set-up, fuel preheat temperature of 100 °C allowed stable operation for long periods of time.

3.2. Effects of the turbine inlet temperature

Experiments and analyses were also performed for different turbine inlet temperatures to obtain a deeper insight into the phenomenology of the combustion of the LW. An interesting trend in CO and THC emissions for diesel fuel and LW is observed in Fig. 6. In the case of LW, it is evident that higher turbine inlet temperatures lower the THC emissions due to postponed reaction quenching and higher reaction rates. This is observed in spite of the higher equivalence ratios that are characteristic for higher TIT resulting in less diluted exhaust gasses. As expected, this trend cannot be identified in the case of diesel fuel at almost identical operating conditions. However, at all TITs much lower absolute values of the THC emissions are characteristic for the diesel fuel. This confirms the fact that low viscosity high cetane number diesel fuel is efficiently burned in the stationary combustion chamber at relatively low bulk temperatures, whereas the increased air flow at higher TIT and thereby altered turbulence conditions in primary zone gradually result in a slight increase of the THC emissions. Mechanisms for decreased THC emissions with the increased TIT in the case of LW were mainly already addressed in the previous section and they can be summarized: (1) Molecular fuel composition: lignin and thereby its decomposition products in LW contain large amounts of cyclic compounds which decrease the autoignition capability of the LW. Higher temperatures are therefore required to ensure high reaction rates of LW that has a low cetane number. (2) Viscosity: high viscosity of the LW deteriorates the atomization quality and the subsequent mixture formation. Higher bulk temperature thus promotes faster evaporation and mixture formation. Both mechanisms reduce negative effects of the short residence time of the combustible mixture that reduces the conversion rate of THC and CO.

The CO emissions follow the same trend as the THC emissions. Both arise from similar mechanisms: high autoignition temperature, low residence time of combustible mixture and reduced atomization quality. The same trend for the CO emissions are reported in [23] where the emissions of a turbine firing waste trap grease dropped substantially with increasing load (increased load translates to increased TIT), whereas for diesel fuel emissions slightly increased with load. This confirms the hypothesis that TIT is a critical parameter in achieving low CO emissions when using LW in gas turbines. CO emissions are also greatly affected by the design of the combustion chamber as was presented in previous (4.1) section. Notable CO emissions can occur through entrapment of CO in liner cooling air or due to operation at incorrect equivalence ratio in the primary zone of combustor. This again is in line with the argument that combustion chamber optimized for the use of LW would further reduce CO emissions. However, changes in dimensions and shape should be performed with care

as this could lower flexibility of the gas turbine and its ability to operate at partial load. CO emissions were below measurable limit in the range of few ppm for operation with diesel fuel due to its high flammability and due to very low equivalence ratios. Elevated CO and THC emissions at fuel preheat temperature of 110 °C became pronounced only at high TIT (800 °C and 850 °C). This is most likely related to the radiative heat transfer to the nozzle. As radiated heat changes with fourth power of temperature, increased combustion temperature contributes to enhanced coking and thus results in poorer atomization of the fuel.

Smoke measurements were below the measurable limit of the experimental equipment for both fuels. Measurement would be possible if less diluted exhaust gasses would be drawn through smoke cell. Low degree of soot formation was also estimated through emission equipment filter. During a 3.5 h operation a sample of exhaust gasses at 3 l/min was drawn through the paper filter. The filtrate was of light brown color, indicating virtually no presence of carbon particles. Brown color is probably characteristic of the ash composition which will be evaluated in the future. For both fuels, the low soot formation can mainly be attributed to the presence of blue flame in proximity of the nozzle, relatively high oxygen supply with the atomizing air and high overall EQR.

NO_x formation is governed by two competing mechanisms. Although Fenimore mechanism is the prevailing one in gas turbine combustors as reported in [26,3], high temperatures promote formation of NO_x through Zeldovich mechanism. Fig. 5 shows increased NO_x emissions at higher TIT for both fuels, which indicates non-negligible NO_x formation rate via the Zeldovich mechanism. In the case of the LW, this thesis is further supported by the fact that LW has a large amount of bound oxygen which should have beneficial impact on lowering of the amount of the nitric oxide obtained through Fenimore mechanism as it is mainly produced in the rich flames through CH radicals [25]. It seems that TIT of around 800 °C represents a limiting value where thermal mechanism starts to prevail. This is also the reason why NO_x emissions are almost equal at 800 °C for diesel fuel. As no oxygen is present in diesel fuel, suppression of Fenimore mechanism cannot occur. At lower TIT, Fenimore mechanism is suppressed when burning LW due to high oxygen concentration and thus NO_x concentration is lower than that of the diesel fuel. At higher TIT the Zeldovich mechanism is responsible for higher NO_x emissions of LW compared to the NO_x emissions of diesel fuel. In the case of LW there is more oxygen available in the high temperature zone which increases the reaction rate for thermal NO_x. NO_x formation through fuel bound nitrogen is relatively unlikely for LW because LW has very low nitrogen content. As for CO and THC, NO_x emissions are also influenced by combustion chamber design and could be lowered if proper measures are used. Higher NO_x emissions for LW in comparison with diesel fuel could also be explained with low soot in the flame which causes less radiation from the flame. Retained heat then promotes thermal NO_x formation [26] as can be seen at high TIT.

Study conducted in [28], where extremely low NO_x emissions were measured when firing glycerol (glycerol has 52% oxygen content) in a high-swirl burner, suggests that NO_x emissions are lower when fuels containing great amount of oxygen are used. Reason for this is probably a widened flame front and consequent reduction in temperatures in the flame zone. This is not the case when burning strongly oxygenated fuels (namely LW) in a gas turbine. The differences can be attributed to the high temperature of the combustion chamber intake air as well as to higher pressures. Burners usually employ combustion air at ambient temperature and this could account for the difference as the majority of NO_x emissions in burners are probably formed through Fenimore mechanism which is effectively suppressed by the fuel bound oxygen. Low intake air temperatures in burners also prevent formation of thermal NO_x which is further reduced by dilution of the flame zone. This happens immediately after fuel molecules start to dissociate and bonded oxygen quickly becomes available resulting in the swiftly diluted flame zone. In case of high pressures, as in gas turbines, this oxygen could also account for the formation of NO_x through N_2O mechanism as it requires three-body reaction. It is clearly visible that the majority (except Fenimore) of NO_x formation mechanisms is promoted in gas turbine firing LW, therefore higher NO_x emissions in comparison to combustion in burners when using similar fuels is expected.

Study with combustion of glycerol [28] show that formaldehyde, acetaldehyde and acetone emissions are comparable with those of fossil fuels. These findings can be partly transferred to liquefied wood as it certainly contains some amount of unreacted glycerol.

4. Conclusions

Paper reports the first results of a successful operation of a gas turbine fueled with a bio-fuel obtained through liquefaction of lignocellulosic materials. Fuel was preconditioned and supplied by a pressurized heated fuel supply line to reduce viscosity of the fuel. Data on feedstock, fuel processing, fuel composition and on the fuel properties are given in the paper to provide the insight into the specifics requirement on the experimental equipment. Fuel properties that mostly influence the requirements on experimental equipment are large amount of bonded oxygen (43%) and low LHV (20.2 MJ/kg) accompanied by high viscosity (540 mPa s @ 40 °C).

Effects of different fuel preheat temperatures and different turbine inlet temperatures were analyzed in the paper. It was shown that elevated fuel temperature results in lower CO and THC emissions. However, care must be taken to avoid possible fuel coking on the fuel nozzle, which deteriorates mixture preparation and has the opposite effect, namely higher CO and THC emissions. Tests in the applied test site revealed that fuel preheat temperature of 100 °C provides an optimum in terms of stable and long term operation as well as low emissions. Emissions concentrations measured, varied according to TIT and fuel preheat temperatures in the following ranges; CO: 159–341 ppm, THC 9–31 ppm, NO_x 50–76 ppm. The lowest emissions were always measured at 100 °C fuel preheat temperature and 850 °C TIT. The analysis shows that even if the CO emissions levels when burning the LW are notably higher than for the diesel fuel, it is expected that with combustion chamber optimized for the LW and with proper fuel conditioning, legislative CO and THC limits could be achieved. It is encouraging that NO_x emissions were sufficiently low, providing margins for further reducing CO and THC emissions by increasing TIT. Reduction of CO and THC emissions is also possible through altering the fuel composition, since increasing the share of cellulose rich feedstock for the liquefaction process reduces the share of ignition resistant hydrocarbons in the fuel.

Since this is an initial study it is not only important to present and analyze the results but also to provide some guidelines for understanding the phenomena that enable further improvements in the fuel processing and in the experimental equipment design with the goal to further reduce exhaust emissions. Fuel properties and fuel processing will be further analyzed to indicate any possibilities to characterize possible precursors for carbonyl emissions. Autoignition temperature and surface tension as well as stability issues will be evaluated. Further, blends with ethanol and emulsions with petroleum derivatives and water will be tested to analyze potential beneficial influences on the exhaust emissions.

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References

[1] Demirbas A. Competitive liquid biofuels from biomass. Appl Energ 2011;88:17–28.
[2] Gupta KK, Rehman A, Sarviya RM. Bio-fuels for the gas turbine: a review. Renew Sustainable Energ Rev 2010;14:2946–55.
[3] Habib Z, Parthasarathy R, Gollahalli S. Performance and emission characteristics of biofuel in a small-scale gas turbine engine. Appl Energ 2010;87:1701–9.
[4] Mohan D, Pittman CU, Steele PH. Pyrolysis of wood/biomass for bio-oil: a critical review. Energ Fuel 2006;20:848–89.
[5] Toor SS, Rosendahl L, Rudolf A. Hydrothermal liquefaction of biomass: a review of subcritical water technologies. Energy 2011;36:2328–42.
[6] Licella Pty Ltd. Fact Sheet – Second gen. bio-crude. Sydney; 2011.
[7] He J, Zhang W. Techno-economic evaluation of thermo-chemical biomass-to-ethanol. Appl Energ 2011;88:1224–32.
[8] Čuk N, Kunaver M, Medved S. Properties of particleboards made by using an adhesive with added liquefied wood. Mater Technol 2011;45:241–5.
[9] Jasiukaityté E, Kunaver M, Strlič M. Cellulose liquefaction in acidified ethylene glycol. Cellulose 2009;16:393–405.
[10] Kobayashi M, Asano T, Kajiyama M, Tomita B. Analysis on residue formation during wood liquefaction with polyhydric alcohol. J Wood Sci 2004;50:407–14.
[11] Jasiukaityté E. Identification of products obtained by acid-catalyzed cellulose and lignin liquefaction with polyfunctional alcohols. Doctoral thesis. Ljubljana: University of Ljubljana, Faculty of chemistry and chemical technology; 2010.
[12] Kunaver M, Jasiukaityté E, Čuk N, Katrašnik T, Rodman Oprešnik S, Seljak T. Biomass waste – an energy source. In: Proceedings of 4th international congress on energy and environment engineering and management. Mérida; 2011.
[13] Kunaver M, Jasiukaityté E, Čuk N, Seljak T, Rodman Oprešnik S, Katrašnik T. Biomass waste: a source of raw materials. In: Book of abstracts of Seventh international conference on renewable resources and. Bruges; 2011.
[14] Rezzoug S, Cappart R. Solvolysis and catalytic hydrotreatement of wood to provide fuel. Biomass Bioenerg 1996;11:343–52.
[15] Kunaver M, Medved S, Čuk N, Jasiukaityté E, Poljanšek I, Strnad T. Application of liquefied wood as a new particle board adhesive system. Bioresource Technol 2010;101:1361–8.
[16] Ji-Lu Z, Yong-Ping K. Spray combustion properties of fast pyrolysis bio-oil produced from rice husk. Energ Convers Manage 2010;51:182–8.
[17] Werkelin J, Skrifvars BJ, Hupa M. Ash-forming elements in four Scandinavian wood species. Part 1: Summer harvest. Biomass Bioenerg 2005;29:451–66.
[18] Jena U, Das KC, Kastner JR. Effect of operating conditions of thermochemical liquefaction on biocrude production from Spirulina platensis. Bioresource Technol 2011;102:6221–9.
[19] European standard BS EN 590:2009. Automotive fuels. Diesel. requirements and test methods.
[20] Kunaver M, Cuk N, Jasiukaityté E, Kovač F, Oprešnik Rodman S, Katrašnik T. Method of producing fuel by liquefaction of cellulose-containing solid materials. Centre of Excellence PoliMat. European pat. appl. no. 11003655.5.
[21] Lefebvre AH, Ballal DR. Gas turbine combustion: alternative fuels and emissions. 3rd ed. Boca Raton: CRC press; 2010.
[22] Chiaramonti D, Oasmaa A, Solantausta Y. Power generation using fast pyrolysis liquids from biomass. Renew Sust Energ Rev 2005;11:1056–86.
[23] Al-Shudeifat MA, Donaldson AB. Combustion of waste trap grease oil in gas turbine generator. Fuel 2010;89:549–53.
[24] Delavan spray technologies, swirl-air nozzles product brochure. Cheshire: Delavan Ltd; 2011.
[25] On board emission measurement system OBS-2200, Instruction Manual. Kyoto: Horiba Ltd; 2005.
[26] Warnatz J, Maas U, Dibble RW. Combustion: physical and chemical fundamentals, modeling and simulation, experiments, pollutant formation. 4th ed. Berlin Heidenberg: Springer-Verlag; 2006.
[27] Sharma NY, Som SK. Influence of fuel volatility and spray parameters on combustion characteristics and NO_x emission in a gas turbine combustor. Appl Therm Eng 2004;24:885–903.
[28] Bohon MD, Metzger BA, Linak WP, King CJ, Roberts WL. Glycerol combustion and emissions. Proc Combustion Ins 2011;33:2717–24.